

## Phase alternation in liquid crystals with terminal phenyl ring

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**Abstract** : A mean-field model for the phase alternation between homologues, as observed in the case of some liquid crystalline homologous series with a terminal phenyl ring, is presented considering the anisotropic interaction of the rigid part and bulky ring of a molecule in the field of other molecules. But the chain interaction is ignored though the chain conformations influence the relative configuration of the other parts. Numerical calculations were done to reproduce the phase diagrams of the phase alternation for the first five members of the homologous series  $\omega$ -phenylalkyl-4-*p*-phenylbenzylidene which is in good agreement with the experimental results.

**Keywords** : Terminal phenyl ring, phase alternations, mean-field theory

**PACS Nos.** : 61.30, 64.70.M

### 1. Introduction

Unusually pronounced even-odd effect in nematic-isotropic transitions has been observed in liquid crystalline compounds with terminal phenyl ring or  $\omega$ -phenylalkyl cinamates [1]. These types of series also show the very interesting behaviour of phase among the homologues. The member of the series with odd number of the methylene units ( $N$ ) in the flexible alkyl chain has both smectic and nematic phases but the same series with even  $N$  has only smectic phase. As a result an alternation of phase occurs [1], because nematic properties are extinguished for odd number of methylene units in the flexible alkyl chain. In an earlier work [2], we formulated a mean-field model by incorporating the effects of the chain conformation explicitly which directly influence the relative configuration of both parts (*viz.*, central rigid part and the terminal phenyl ring) and as a result the longitudinal polarizability of the molecules is changed. This model has made it possible for us to

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reproduce the unusually pronounced even-odd effect in  $N - I$  transition. In this communication we present an extension of the earlier model to the smectic phase by introducing a pure translational McMillan parameter [3]. Conformational and dispersive energies for the rigid part and the terminal ring of a molecule in the field of the other molecules are considered. Numerical calculations have been done on the homologous series  $\omega$ -phenylalkyl-4-*p*-phenyl benzylidene for the first five member of the series. The calculation reproduces the phase alternation behaviour which is observed in the experimental phase diagram of that series.

## 2. Method

Following reference 2, we consider the mean-field experienced by a molecule to consist of three parts—one for the rigid core ( $E_a$ ), the other for the end phenyl ring ( $E_b$ ) and the conformation energy of the chain segment ( $E_{\text{conf}}$ ). For simplification, we ignored the contribution of chain part to the mean-field as it is small compared to the other contribution. Before writing the energy expression let us state the definitions of the order parameters to be used.

Orientalional order parameter for the rigid parts

$$\eta_a = \langle P_2(\cos \theta_a) \rangle, \quad (1)$$

where  $\theta_a$  is the angle between the rigid part and the mean-field direction.  $\langle \rangle$  means a statistical average.

The phenyl ring order can be defined as

$$\eta_b = \langle P_2(\cos \theta_b(\phi)) \rangle, \quad (2)$$

where  $\theta_b$  is the polar angle between the phenyl ring and the direction of the field.  $\phi$  is the angle of rotation of the ring about the rigid part.

The translational order parameter

$$\tau = \left\langle \cos\left(\frac{2\pi z}{d}\right) \right\rangle, \quad (3)$$

where  $d$  is the layer spacing and  $z$  is chosen along the layer normal.

Then the energies can therefore be written as,

$$E_a = - \left[ V_{aa} \frac{C_a(n)}{V_a} \eta_a + V_{ab} \frac{C_b(n)}{V_b} \eta_b \right] P_2(\cos \theta_a) - \left[ V_{aa} \frac{C_a(n)}{V_a} + V_{ab} \frac{C_b(n)}{V_b} \right] \tau \cos\left(\frac{2\pi z}{d}\right), \quad (4)$$

$$E_b = - \left[ V_{ab} \frac{C_a(n)}{V_a} \eta_a + V_{bb} \frac{C_b(n)}{V_b} \eta_b \right] P_2(\cos \theta_b(\phi)) \quad (5)$$

and 
$$E_{\text{conf}} = \sum_{i=2}^N U(\xi_{i-1}, \xi_i) \quad (6)$$

In the above expressions the suffixes 'a' and 'b' have been introduced to denote entities pertaining to rigid and phenyl parts of a molecule respectively.  $C_a(N)$  and  $C_b(N)$  are the respective volume fractions of the  $N$ -th member of the homologous series and  $V_a$ ,  $V_b$  are the molecular volumes of the two basic components. The volumes of the different parts are estimated from the table values for molecular weight and density data of the sample.  $V_{aa}$ ,  $V_{bb}$  and  $V_{ab}$  are the coupling constants for the interaction mean field with the first suffix representing the component molecule that experiences the mean field and the latter suffix indicating the mean field producing agent. By analogy with the result for the binary-mixtures of nematogenic molecules [4], we have

$$V_{ab} = \sqrt{V_{aa}V_{bb}}$$

Therefore, only two of the coupling constants remain as adjustable parameters, which are fixed from the nematic-isotropic transition temperature of two homologues, as explained in reference 2. The parameter  $\delta$  is the relative coupling strength of the Kobayashi two-particle potential [5] which is constant for a homologous series and also temperature independent. The value of this parameter is obtained by using the value of the smectic to nematic/isotropic transition temperature of the homologue. Here we assume that the correlation between the orientation order and translation order is very weak. Hence the mixed parameter term in the model potential is neglected.  $U$  is the internal energy of  $i$ -th segment of a chain and  $\xi$  represents any of the three rotation isomer states namely  $t$ (trans),  $g^+$ (gauche). The value of these states are given in reference [6]. The values of the order parameters at a particular temperature  $T$  can be obtained by full self-consistent solutions of the following equations :

$$\eta_a = \frac{1}{Z_0} \sum_{\text{all conf}} \int_0^d \int_0^{2\pi} \int_0^1 P_2(\cos \theta_a) \exp [E/kT] d(\cos \theta) d\phi dz \quad (7)$$

$$\eta_b = \frac{1}{Z_0} \sum_{\text{all conf}} \int_0^d \int_0^{2\pi} \int_0^1 P_2(\cos \theta_b(\phi)) \exp [E/kT] d(\cos \theta) d\phi dz \quad (8)$$

$$\tau = \frac{1}{Z_0} \sum_{\text{all conf}} \int_0^d \int_0^{2\pi} \int_0^1 \cos\left(\frac{2\pi z}{d}\right) \exp [E/kT] d(\cos \theta) d\phi dz \quad (9)$$

where  $Z_0$  is the partition function of the system in ordered phase at a particular temperature  $T$  and it is given by,

$$Z_0 = \sum_{\text{all conf}} \int_0^d \int_0^{2\pi} \int_0^1 \exp [E/kT] d(\cos \theta) d\phi dz$$

For each temperature, the self-consistent solution of the order parameters is found and the stable solution is picked up corresponding to the minimum of the Helmholtz free energy per particle. The expression for this free energy is given as,

$$F = \frac{0.5}{V_a + V_b} [V_{aa}(\eta_a^2 + \delta\tau^2) + V_{ab}(2\eta_a\eta_b + \delta\tau^2) + V_{bb}\eta_b^2] - kT \ln [Z_o / Z_i] \quad (10)$$

where  $Z_i$  is the partition function in isotropic phase.

### 3. Result and discussion

The calculated transition temperatures of the homologous series  $\omega$ -phenyl alkyl-4-*p*-phenyl- benzylidene are compared with the experimentally observed value in Figure 1. The estimated volumes are,  $V_a = 433.91 \text{ \AA}^3$ ,  $V_b = 108.48 \text{ \AA}^3$ , together with the volume for the each chain segment  $27 \text{ \AA}^3$ . The values of the coupling constants  $V_{aa}$ ,  $V_{bb}$  and  $V_{ab}$  are 2059950.0, 22162.85 and 213668.82 respectively in C G S unit. The value of  $\delta$  is 0.37. It is to be noted that the ratio of the strength parameters are constant throughout the nematic phase and independent of the number of the homologue whose value is 9.64.

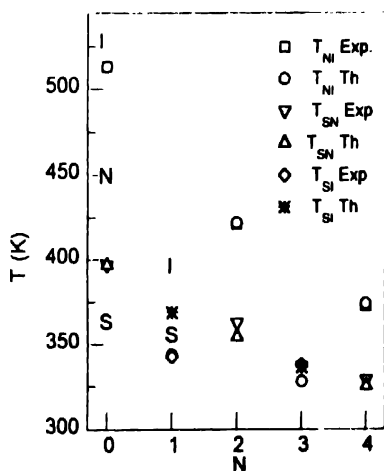


Figure 1. Plot of transition temperature ( $T$ ) against number of methylene groups ( $N$ ) in the chain.

In conclusion, we would like to mention that this is possibly the first calculation where the generally observed feature of the cinnamate homologous series, namely the phase alteration is well reproduced. The calculated transition points are seem to be only about 10 – 15 K off the experimental values. This small deviation may be due to the steric effect which has not been considered directly into our model potential expression. As the molecules are packed in a layer in the smectic phase there is considerable lateral steric repulsion between the molecules [7]. It is quite likely that those conformations for which the chain segments deviate much from the molecular axis are suppressed due to the lateral repulsion by the neighbouring molecules. Further efforts should be made for better agreement with experiments.

### Acknowledgments

We are grateful to Prof. M K Roy and Prof. M Saha for their valuable comments and suggestions. One of us (J Saha) wishes to thank the Council of Scientific and Industrial Research, India for the Research Associateship offered to her.

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